

6. $4f^n \Rightarrow 4f^{n-1}5d$. Examples are Ce^{3+} , Pr^{3+} , Sm^{2+} , Eu^{2+} , Tm^{2+} , and Yb^{2+} . Only absorption transitions are observed for Tb^{3+} .
7. A charge-transfer transition or a transition between an anion p electron and an empty cation orbital. Examples are intramolecular transitions in complexes such as VO_4^{3-} , WO_4^{2-} , and MoO_4^{2-} . More specifically, typical examples are a transition from the $2p$ orbital of O^{2-} to the $3d$ orbital of V^{5+} in VO_4^{3-} , and transitions from $\text{O}^{2-}(2p)$ or $\text{S}^{2-}(3p)$ to $\text{Yb}^{3+}(4f)$. Transitions from anion p orbitals to Eu^{3+} or transition metal ions are observed only as absorption processes.
8. $\pi \Rightarrow \pi^*$ and $n \Rightarrow \pi^*$. Organic molecules having π electrons make up this group. The notation n indicates a nonbonding electron of a heteroatom in an organic molecule.

2.3.2 Configurational coordinate model¹⁻⁵

2.3.2.1 Description by a classical model

The configurational coordinate model is often used to explain optical properties, particularly the effect of lattice vibrations, of a localized center. In this model, a luminescent ion and the ions at its nearest neighbor sites are selected for simplicity. In most cases, one can regard these ions as an isolated molecule by neglecting the effects of other distant ions. In this way, the huge number of actual vibrational modes of the lattice can be approximated by a small number or a combination of specific normal coordinates. These normal coordinates are called the *configurational coordinates*. The *configurational coordinate model* explains optical properties of a localized center on the basis of potential curves, each of which represents the total energy of the molecule in its ground or excited state as a function of the configurational coordinate (Figure 12). Here, the total energy means the sum of the electron energy and ion energy.

To understand how the configurational coordinate model is built, one is first reminded of the adiabatic potential of a diatomic molecule, in which the variable on the abscissa is simply the interatomic distance. In contrast, the adiabatic potential of a polyatomic molecule requires a multidimensional space, but it is approximated by a single configurational coordinate in the one-dimensional configurational coordinate model. In this model, the totally symmetric vibrational mode or the "breathing mode" is usually employed. Such a simple model can explain a number of facts qualitatively, such as:

1. Stokes' law; i.e., the fact that the energy of absorption is higher than that of emission in most cases. The energy difference between the two is called the Stokes' shift.
2. The widths of absorption or emission bands and their temperature dependence.
3. Thermal quenching of luminescence. It must be remarked, however, that the one-dimensional model gives only a qualitative explanation of thermal quenching. A quantitatively valid explanation can be obtained only by a multidimensional model.⁶

Following the path of the optical transition illustrated in Figure 12, presume that the bonding force between the luminescent ion and a nearest-neighbor ion is expressed by Hooke's law. The deviation from the equilibrium position of the ions is taken as the configurational coordinate denoted as Q . The total energy of the ground state, U_g , and that of the excited state, U_e , are given by the following relations.

$$U_g = K_g \frac{Q^2}{2} \quad (73a)$$

Figure 12 A scheme modified by representation. $C \Rightarrow D$ indicate

where K_g and K_e at the equilibrium

The spatial excited states, ξ boring ions. The force constant the excited state orbital depend has less curvature

In Figure broken arrows mately at the s Condon principle heavier than at the equilibrium probability for 10^{13} s^{-1} , while relaxes to the emission process temperature, t

Only absorption

electron and an
mplexes such as
a transition from
ons from $O^{2-}(2p)$
transition metal

this group. The
rganic molecule.

properties, particu-
luminescent ion
st cases, one can
her distant ions.
be approximated
se normal coor-
te model explains
, each of which
as a function of
the sum of the

is first reminded
n the abscissa is
polyatomic mol-
configurational
this model, the
employed. Such

that of emission
Stokes' shift.
e dependence.
er, that the one-
al quenching. A
ensional model.⁶

resume that the
is expressed by
is taken as the
d state, U_g , and

(73a)

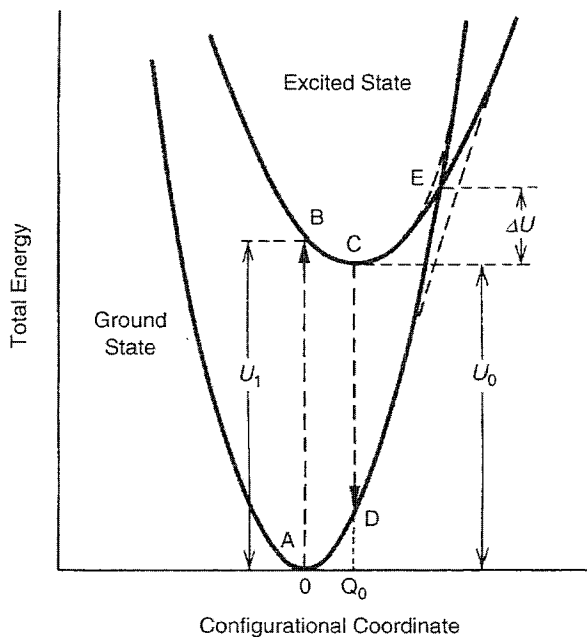


Figure 12 A schematic illustration of a configurational coordinate model. The two curves are modified by repulsion near the intersection (broken lines). The vertical broken lines $A \rightleftharpoons B$ and $C \rightleftharpoons D$ indicate the absorption and emission of light, respectively.

$$U_e = K_e \frac{(Q - Q_0)^2}{2} + U_0 \quad (73b)$$

where K_g and K_e are the force constants of the chemical bond, Q_0 is the interatomic distance at the equilibrium of the ground state, and U_0 is the total energy at $Q = Q_0$.

The spatial distribution of an electron orbital is different between the ground and excited states, giving rise to a difference in the electron wavefunction overlap with neighboring ions. This difference further induces a change in the equilibrium position and the force constant of the ground and excited states, and is the origin of the Stokes' shift. In the excited state, the orbital is more spread out, so that the energy of such an electron orbital depends less on the configuration coordinate; in other words, the potential curve has less curvature.

In Figure 12, optical absorption and emission processes are indicated by vertical broken arrows. As this illustration shows, the nucleus of an emitting ion stays approximately at the same position throughout the optical processes. This is called the Franck-Condon principle. This approximation is quite reasonable since an atomic nucleus is heavier than an electron by 10^3 to 10^5 times. At 0K, the optical absorption proceeds from the equilibrium position of the ground state, as indicated by the arrow $A \rightarrow B$. The probability for an excited electron to lose energy by generating lattice vibration is 10^{12} to 10^{13} s^{-1} , while the probability for light emission is at most 10^9 s^{-1} . Consequently, state B relaxes to the equilibrium position C before it emits luminescence. This is followed by the emission process $C \rightarrow D$ and the relaxation process $D \rightarrow A$, completing the cycle. At finite temperature, the electron state oscillates around the equilibrium position along the con-

figural coordinate curve up to the thermal energy of kT . The amplitude of this oscillation causes the spectral width of the absorption transition.

When two configurational coordinate curves intersect with each other as shown in Figure 12, an electron in the excited state can cross the intersection E assisted by thermal energy and can reach the ground state nonradiatively. In other words, one can assume a nonradiative relaxation process with the activation energy ΔU , and with the transition probability per unit time N given by:

$$N = s \exp \frac{-\Delta U}{kT} \quad (74)$$

where s is a product of the transition probability between the ground and excited states and a frequency, with which the excited state reaches the intersection E. This quantity s can be treated as a constant, since it is only weakly dependent on temperature. It is called the *frequency factor* and is typically of the order of 10^{13} s^{-1} .

By employing Eq. 74 and letting W be the luminescence probability, the luminescence efficiency η can be expressed as:

$$\eta = \frac{W}{W + N} = \left[1 + \frac{s}{W} \exp \frac{-\Delta U}{kT} \right]^{-1} \quad (75)$$

If the equilibrium position of the excited state C is located outside the configurational coordinate curve of the ground state, the excited state intersects the ground state in relaxing from B to C, leading to a nonradiative process.

It can be shown by quantum mechanics that the configurational coordinate curves can actually intersect each other only when the two states belong to different irreducible representations. Otherwise, the two curves behave in a repulsive way to each other, giving rise to an energy gap at the expected intersection of the potentials. It is, however, possible for either state to cross over with high probability, because the wavefunctions of the two states are admixed near the intersection. In contrast to the above case, the intersection of two configurational coordinate curves is generally allowed in a multidimensional model.

2.3.2.2 Quantum mechanical description

The classical description discussed above cannot satisfactorily explain observed phenomena, e.g., spectral shapes and nonradiative transition probabilities. It is thus necessary to discuss the configurational coordinate model based on quantum mechanics.

Suppose that the energy state of a localized center involved in luminescence processes is described by a wavefunction Ψ . It is a function of both electronic coordinates \mathbf{r} and nuclear coordinates \mathbf{R} , but can be separated into the electronic part and the nuclear part by the *adiabatic approximation*:

$$\Psi_{nk}(\mathbf{r}, \mathbf{R}) = \psi_k(\mathbf{r}, \mathbf{R}) \chi_{nk}(\mathbf{R}) \quad (76)$$

where n and k are the quantum numbers indicating the energy states of the electron and the nucleus, respectively. For the nuclear wavefunction $\chi_{nk}(\mathbf{R})$, the time-independent Schrödinger equation can be written as follows:

Total Energy

Figure 13 Discrete wavefunctions ψ_0^a at the frequency at the

with α being the \mathbf{R}_ω and E_{nk} the total energy of two parts: the nuclear energy and the electronic energy. The term is the first nuclear coordinate or a vibrational coordinate.

Consider a harmonic oscillator with discrete energy levels. Figure 13.

where ω is the pr